

AIR RESOURCES BOARD

2020 L STREET
P.O. BOX 2815
SACRAMENTO, CA 95812



MEMORANDUM

TO: *John*
John Sanders, Ph.D., Chief
Environmental Monitoring and
Pest Management Branch
Department of Pesticide Regulation

FROM: *Genevieve Shiroma*
Genevieve A. Shiroma, Chief
Air Quality Measures Branch

DATE: March 30, 1995

SUBJECT: AIR RESOURCES BOARD MONITORING OF AZINPHOS METHYL

In response to a Department of Pesticide Regulation request, the Air Resources Board staff conducted application site monitoring in Glenn County for azinphos methyl. The results and additional background information are included in the enclosures to this memorandum. A chronology of events is included in Enclosure I. The complete application site monitoring results are included in Enclosure II.

If you have questions regarding the actual field sampling and analysis, please contact Mr. George Lew, Chief, Engineering and Laboratory Branch, at (916) 263-1630. For other questions, please contact me at (916) 322-7072.

Enclosures

cc: James Stratton, M.D., M.P.H. (w/Enclosures)
Interim Director
Office of Environmental Health Hazard Assessment

Mr. Ed Romano (w/Enclosures)
Glenn County Agricultural Commissioner/
Air Pollution Control Officer
720 North Colusa Street
Post Office Box 351
Willows, California 95988

Ms. Loreen Kleinschmidt (w/Enclosures)
Library Assistant
Department of Environmental Toxicology
University of California, Davis

Mr. George Lew, Chief
Engineering and Laboratory Branch
Monitoring and Laboratory Division

AIR RESOURCES BOARD

2020 L STREET
P.O. BOX 2815
SACRAMENTO, CA 95812



March 30, 1995

Mr. Dave Keyawa
Supervisor
Keyawa Orchards, Inc.
Post Office Box 8270
Chico, California 95927

Dear Mr. Keyawa:

Enclosed is a copy of the final report for the application site monitoring for azinphos methyl conducted by the Air Resources Board staff in July, 1994 on property of the Keyawa Orchards, Inc. Your cooperation and assistance are greatly appreciated, and allowed us to collect data needed for the Department of Pesticide Regulation's (DPR) toxic air contaminant program. State law requires the DPR to evaluate airborne pesticides which may pose hazards to human health.

If you have any questions about the report, please call Mr. George Lew, Chief, Engineering and Laboratory Branch, Monitoring and Laboratory Division, at (916) 263-1630.

Sincerely,

A handwritten signature in cursive script that reads 'Genevieve Shiroma'.

Genevieve A. Shiroma, Chief
Air Quality Measures Branch

Enclosure

cc: Mr. Ed Romano
Glenn County Agricultural Commissioner
720 North Colusa Street
Post Office Box 351
Willows, California 95988

✓John Sanders, Ph.D., Chief
Environmental Monitoring and
Pest Management Branch
Department of Pesticide Regulation
1020 N Street, Room 161
Sacramento, California 95814

Mr. George Lew
Chief, Engineering and Laboratory Branch
Monitoring and Laboratory Division

Enclosure I
Chronology of Events

Azinphos methyl Monitoring
Chronology of Major Events

August, 1986	DPR transmits to ARB monitoring recommendations for azinphos methyl.
January, 1988	ARB transmitted to DPR the ambient monitoring report for azinphos methyl.
May, 1988	DPR transmitted a request for application site monitoring for azinphos methyl.
July, 1994	ARB transmitted to DPR the plan for application site monitoring of azinphos methyl in Glenn County.
July 28 - August 1, 1994	Application site monitoring conducted in Glenn County for azinphos methyl.

Enclosure II

Report on Ambient Concentrations near an Application
of Azinphos methyl in Glenn County

State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

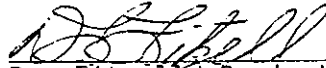
AMBIENT AIR MONITORING AFTER AN APPLICATION OF AZINPHOS METHYL
IN GLENN COUNTY DURING JULY 1994

Engineering and Laboratory Branch
Monitoring and Laboratory Division

Test Report No. C93-061A

Report Date: March 1, 1995

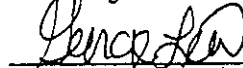
APPROVED:



Don Fitzell, Project Engineer



Peter K. Ouchida, Manager,
Testing Section



George Dew, Chief,
Engineering and Laboratory Branch

This report has been reviewed by the staff of the Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Ambient Air Monitoring After an Application of Azinphos Methyl
in Glenn County During July 1994

This report presents the results of ambient air monitoring after an aerial application by helicopter of azinphos methyl at a selected walnut orchard in Glenn County. Samples were collected before, during and for 72 hours after the application. Only samples collected during the application had levels above the detection limit (0.10 ug/sample or 0.076 ug/m³ for a 12-hour sample). The values detected during this 3-hour sampling period ranged from 0.69 ug/m³ to 1.7 ug/m³.

Acknowledgments

Jack Rogers was the Instrument Technician. Bill Duckworth of the Glenn County Agricultural Commissioner's Office arranged for a suitable orchard to monitor. Assistance was also provided by Lynn Baker and Ruth Tomlin of the ARB's Air Quality Measures Branch.

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Ambient Air Monitoring After an Application of Azinphos Methyl
in Glenn County During July 1994

I. INTRODUCTION

The Air Resources Board (ARB) Engineering and Laboratory Branch (ELB) conducted a three-day source impacted ambient monitoring program for an application of azinphos methyl (Guthion) to a walnut orchard in Glenn County during July of 1994. This monitoring was performed at the request of the California Department of Pesticide Regulation (DPR) and the ARB Air Quality Measures Branch (AQMB). This monitoring occurred from July 28 through August 1, 1994. As required by the Food and Agricultural Code Section 14021, this monitoring was conducted to provide DPR with data for the evaluation of the persistence and exposure of airborne pesticides.

II. DESCRIPTION

Azinphos methyl (molecular weight 317.34 g/mole) is a colorless crystalline solid at room temperature with a melting point of 72.4°C. It has a vapor pressure of 1.8×10^{-6} mbar at 20 °C. It is soluble in n-hexane, dichloromethane, 2-propanol and toluene. The (rat) Oral LD₅₀ is approx. 10 mg/kg and the Dermal LD₅₀ is approx. 200 mg/kg.

Azinphos methyl is an organophosphorus pesticide used on a wide variety of crops such as: fruits, nuts, vegetables, field crops, shade trees and ornamentals. It is a restricted use material under Section 6400, Title 3 of the California Code of Regulations. The Pesticide Use Report for 1992 indicates azinphos methyl is most widely used on almonds (236,811 pounds), walnuts (74,741 pounds) pears (67,230 pounds) and apples (46,634 pounds).

III. SAMPLING LOCATIONS

A walnut orchard of about 118 acres was selected (FIGURE I) by Bill Duckworth of the Glenn County Agricultural Commissioner's Office for application monitoring. Four samplers were set up (see FIGURE II): one on the eastern perimeter (site E) at a distance of about 15 yards from the orchard, one about 20 yards from the southern perimeter (site S), one about 25 yards from the northern perimeter (site N) and one near the western side of the orchard (site W). Site W was actually on a levee road within the orchard. It was impossible to set up a sampler

on the western perimeter of the orchard because of the Sacramento River. The helicopter did not release azinphos methyl over the levee road nor over Road XX. A meteorological station to determine wind speed and direction was set up adjacent to site S. Sites S and N each took duplicate samples while sites E and W took single samples.

The application was by helicopter and took about 1 hour. The first passes were along the eastern edge where bee hives were near the orchard. After that the azinphos methyl was applied from east to west, beginning at the northeast corner. Azinphos methyl was the only product applied to the field at this time. The formulation was Guthion Solupak (50% active ingredient) and was applied at a rate of 4 pounds in 30 gallons of water per acre. The Restricted Materials Permit, Notice of Intent and Pesticide Use Report are in APPENDIX I.

IV. SAMPLING METHODOLOGY

The Standard Operating Procedure (S.O.P.) for this pesticide (see APPENDIX II) requires passing measured quantities of ambient air through a Teflon filter followed by XAD-2 resin contained in a glass tube. It was incorrectly assumed that all of the azinphos methyl was recovered from the XAD-2 resin in the earlier ambient study, so only the resin tubes were used for this study. Subsequent to sampling, it was necessary to verify the efficiency of XAD-2 resin tubes (without Teflon filter) for the collection of azinphos methyl through additional QA/QC work done after the samples were analyzed (see RESULTS).

The tubes are 8 mm x 110 mm, with 400 mg in the primary section and 200 mg in the secondary (SKC catalog #226-09). Any azinphos methyl present in the sampled ambient air is expected to be captured by the resin contained in the tubes. Subsequent to sampling, the tubes were stored on ice until delivery to the laboratory and then stored in a freezer until analysis was complete.

Sampling trains designed to operate continuously were set up at the four sampling sites identified in FIGURE II. Duplicate samples were obtained from sites N and S, all duplicates were analyzed. The sampling schedule outlined in the QA Plan (APPENDIX III, Attachment II) was modified so that the sample tubes did not have to be changed in the middle of the night.

Each sample train consisted of an XAD-2 resin tube with tube cover, Teflon fittings and tubing, rain shield, flow meter with valve, train support, and a 12VDC battery-powered vacuum pump. A diagram of the sampling train is shown in APPENDIX III, Attachment I. The tubes were placed approximately 1.5 meters above the ground. Each tube was prepared for use by breaking off each sealed glass end and then immediately inserting the tube into a Teflon fitting. The tubes were oriented in the sampling train according to a small arrow printed on

the side of each tube indicating the direction of flow. Covers were placed around the tube to protect the adsorbent from exposure to sunlight.

The sample pump was started and the flow through a rotometer adjusted with a metering valve to an indicated reading of 2.0 liters per minute (lpm). A leak check was performed by blocking off the sample inlet. The sampling train would be determined to be leak-free, if the indicated flow dropped to zero. Upon completion of a successful leak check, the indicated flow rate was again set at 2.0 lpm and was recorded (if different from the planned 2.0 lpm) along with date, time, and site location. Calibration prior to use in the orchard indicated that an average flow rate of 1.8 lpm was actually achieved when the rotometers were set to 2.0 lpm. This average flow rate was used to calculate all sample volumes.

At the end of each sampling period the final indicated flow rate (if different than the set 2.0 lpm), the stop date and time were recorded. The XAD-2 tubes were then removed from the sample train, end caps installed on both ends, and identification labels affixed to each tube. Each tube was then placed in a culture tube with a screw cap and stored with ice in a covered chest while in the field. Samples were stored in a freezer in Sacramento until analysis was completed.

V. ANALYTICAL METHODOLOGY

The XAD-2 resin tubes recovered from each sampler were analyzed by the ELB staff. The XAD-2 resin in the primary section of each sample tube was extracted with 2 ml isooctane:acetone (80:20) followed by gas chromatographic (GC) analysis using a 30 m x 0.25 mm i.d., 0.25 μ m film DB-1 column and a nitrogen/phosphorus detector (NPD) (see APPENDIX II for detailed method). All samples were analyzed within two weeks of collection. No back up sections of the tubes was analyzed since the field samples were all below the level used for the laboratory QC studies (TABLE IV).

VI. RESULTS

The monitoring results are shown in TABLE I. A summary of the on-site meteorological data is presented in TABLE II. A summary of the monitoring and meteorological data is presented in TABLE III. The laboratory quality control data is presented in TABLE IV. Additional detailed meteorological data from the California Irrigation Management Information System (CIMIS) station, located in Orland, is presented in APPENDIX IV. None of the results presented in this report have been corrected for percentage recovery.

TABLE III is an attempt to graphically present the meteorological data and the levels of azinphos methyl detected at the various sites. As TABLE I shows, low levels of azinphos methyl were found and only during the period of application. The concentrations determined ranged from 0.69 ug/m³ to 1.7 ug/m³. This is obviously due to the low volatility of this insecticide.

The laboratory quality control data (TABLE IV) indicates good results. The lowest recovery was for the field spikes and these averaged 80%. While Teflon filters may be the method of choice, the data clearly indicate that no losses occurred with the use of the XAD-2 resin tubes. This study shows that XAD-2 resin by itself is an appropriate collection medium.

The results for the laboratory audit by ARB's Quality Management and Operations Support Branch (QMOSB) are shown in TABLE IV. The laboratory's values were consistently low (-31.7%) compared to the spiked value. This clearly indicates a systematic error, either in the preparation of the laboratory's standards or the audit spikes. Because the detected values from the field samples were low and only during the application period, no attempt was made to resolve this discrepancy.

VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability are described in the Standard Operating Procedure for azinphos methyl (APPENDIX II).

Most of the procedures outlined in the Quality Assurance Plan (APPENDIX III, Attachment II) were followed. The only exception was a slight modification of the sampling schedule (see SAMPLING METHODOLOGY). In addition, a flow rate audit, a systems audit and an analytical performance audit were performed by the QMOSB (see APPENDIX V).



FIGURE 11. Azinphos Methyl Monitoring Sites



TABLE I. Azinphos Methyl Application Monitoring Data

Sample ID	Time (min.)	Volume* (m ³)	Total (ug)	Concentration (ug/m ³)	Collection Time (Approx.)
OW	210	0.39	ND	--	Background
ON	210	0.39	ND	--	
OS	205	0.38	ND	--	7/28/94
OE	210	0.39	ND	--	(1400-1800)
1W	145	0.27	0.42	1.6	(Application)
1N-1	160	0.29	0.50	1.7	
1N-2	160	0.29	0.34	1.2	
1S-1	155	0.29	0.20	0.69	
1S-2	155	0.29	0.25	0.86	7/29/94
1E	165	0.30	0.44	1.5	(0600-0900)
2W	110	0.20	ND	--	
2N-1	100	0.18	ND	--	
2N-2	100	0.18	ND	--	
2S-1	110	0.20	ND	--	
2S-2	110	0.20	ND	--	7/29/94
2E	105	0.19	ND	--	(0900-1030)
3W	240	0.44	ND	--	
3N-1	240	0.44	ND	--	
3N-2	240	0.44	ND	--	
3S-1	240	0.44	ND	--	
3S-2	240	0.44	ND	--	
3E	240	0.44	ND	--	7/29/94
3B	BLANK	--	ND	--	(1030-1430)

*All flows at 1.8 liters per minute (see SAMPLING METHODOLOGY).

ND = Not Detected, <0.1 ug/sample.

No values corrected for percentage of recovery.

TABLE I. Azinphos Methyl Application Monitoring Data (cont.)

Sample	Time	Volume*	Total	Concentration	Collection Time
ID	(min.)	(m ³)	(ug)	(ug/m ³)	(Approx.)
4W	300	0.55	ND	--	
4N-1	295	0.54	ND	--	
4N-2	295	0.54	ND	--	
4S-1	295	0.54	ND	--	
4S-2	295	0.54	ND	--	
4E	295	0.54	ND	--	7/29/94 (1430-1930)
5W	720	1.3	ND	--	
5N-1	720	1.3	ND	--	
5N-2	720	1.3	ND	--	
5S-1	720	1.3	ND	--	
5S-2	720	1.3	ND	--	7/29-30/94
5E	725	1.3	ND	--	(1930-0730)
6W	1460	2.7	ND	--	
6N-1	1465	2.7	ND	--	
6N-2	1465	2.7	ND	--	
6S-1	1465	2.7	ND	--	
6S-2	1465	2.7	ND	--	7/30-31/94
6E	1460	2.7	ND	--	(0730-0730)
7W	1400	2.6	ND	--	
7N-1	1385	2.5	ND	--	
7N-2	1385	2.5	ND	--	
7S-1	1390	2.6	ND	--	
7S-2	1390	2.6	ND	--	7/31-8/1/94
7E	1370	2.5	ND	--	(0730-0730)

* All flows at 1.8 liters per minute (see SAMPLING METHODOLOGY).

ND = Not Detected, <0.1 ug/sample.

No values corrected for percentage of recovery.

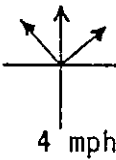
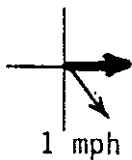
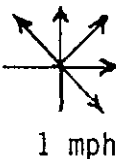
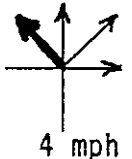
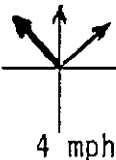
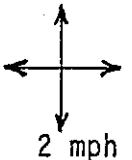

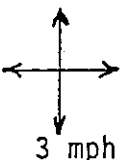
TABLE II. Azinphos Methyl Meteorological Data

Sampling Period	Wind* Direction	Wind Speed (mph)
0	SE/S/SW	4
1	<u>W</u> /NW	1
2	SE/S/SW/W/NW	1
3	<u>SE</u> /SW/S/W	4
4	<u>SE</u> /S/SW	4
5	N/S/E/W	2
6	S/NW/W	2
7	N/S/E/W	3

BOLD indicates predominant wind direction, if any.

*Indicates direction wind blows from.

TABLE III. Summary of Azinphos Methyl Application Data ($\mu\text{g}/\text{m}^3$)

<p>(0) [N] <u>ND</u></p> <p>[W] <u>ND</u>  [E] <u>ND</u></p> <p>[S] <u>ND</u></p> <p>4 mph</p>	<p>[N] <u>1.4*</u></p> <p>(1) [W] <u>1.6</u>  [E] <u>1.5</u></p> <p>[S] <u>0.78*</u></p> <p>1 mph</p>
<p>(2) [N] <u>ND</u></p> <p>[W] <u>ND</u>  [E] <u>ND</u></p> <p>[S] <u>ND</u></p> <p>1 mph</p>	<p>[N] <u>ND</u></p> <p>(3) [W] <u>ND</u>  [E] <u>ND</u></p> <p>[S] <u>ND</u></p> <p>4 mph</p>
<p>(4) [N] <u>ND</u></p> <p>[W] <u>ND</u>  [E] <u>ND</u></p> <p>[S] <u>ND</u></p> <p>4 mph</p>	<p>[N] <u>ND</u></p> <p>(5) [W] <u>ND</u>  [E] <u>ND</u></p> <p>[S] <u>ND</u></p> <p>2 mph</p>
<p>(6) [N] <u>ND</u></p> <p>[W] <u>ND</u>  [E] <u>ND</u></p> <p>[S] <u>ND</u></p> <p>2 mph</p>	<p>[N] <u>ND</u></p> <p>(7) [W] <u>ND</u>  [E] <u>ND</u></p> <p>[S] <u>ND</u></p> <p>3 mph</p>

* Average of two collocated samples.
 () Indicates sampling period. [] Indicates sampling site represented.
 Arrow indicates direction wind is blowing toward. Bold indicates predominant wind direction, if any.
 ND = not detected, less than the limit of quantitation, $0.3 \mu\text{g}/\text{sample}$.

TABLE IV. Laboratory Quality Control Data

ID	Amount Spiked	Amount Recovered	Percent Recovered	Number of Replicates
DS	1.83 ug	1.87 ug	102.0	2
LS	1.83 ug	1.71 ug	93.4	2
CC	1.83 ug	1.54 ug	84.2	2
FS	1.83 ug	1.46 ug	80.0	3
AZM-1	0.832 ug	0.56 ug	67.3	2
AZM-2	0.312 ug	0.22 ug	70.5	2
AZM-3	0.000 ug	ND	--	2
AZM-4	0.520 ug	0.34 ug	65.4	2
AZM-5	0.312 ug	0.21 ug	67.3	2
AZM-6	0.832 ug	0.55 ug	66.1	2
AZM-7	0.520 ug	0.38 ug	73.1	2

ND = Not detected, <0.1 ug/sample.

DS = Direct spike. The azinphos methyl was delivered directly into the same type of vial used for extraction. Two ml of solvent was added then an aliquot transferred to a sample vial for analysis.

LS = Laboratory spike. The azinphos methyl was added to the front of the primary section of an XAD tube and allowed to air dry for approx. 20 minutes. It was then extracted and analyzed as a field sample.

CC = Collection/conversion. The azinphos methyl was added to the front of the primary section of an XAD tube then was placed in a sample train (in Sacramento) and had air pulled through it for 21 hours. It was then extracted and analyzed as a field sample.

FS = Field spike. The azinphos methyl was added to the front of the primary section of an XAD tube. It was taken into the field in an ice chest and stored with the regular field samples. It was then extracted and analyzed as a field sample.

AZM- = Azinphos methyl audit spike prepared by ARB's QMOSB.